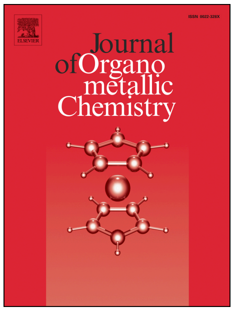

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Synthesis and Solution Behaviour of Metal-Carbonyl Amphiphiles with an Fp ($CpFe(CO)_2$) Junction

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Abstract

Metallo-amphiphilic macromolecules with an iron-carbonyl junction ($PEGPPh_2$-FpR, $PEGPPh_2$: polyethylene glycol diphenyl phosphine, $M_{n, PEG}$ = 550 or 2000 g/mol; R = octadecyl or hexyl; Fp = $CpFe(CO)_2$) are synthesized *via* migration insertion reaction of FpR in the presence of $PEGPPh_2$ and are characterized using ^{31}P, ^{1}H NMR and IR. The prepared amphiphiles are air stable, soluble in most organic solvents, e.g. THF, DCM, DMF, and exhibit a reversible redox activity as indicated by cyclic voltammetry (CV) experiments. Surface tension measurements indicate that the prepared molecules exhibit typical amphiphilic properties with critical micelle concentrations (CMC) in water ranging between 30 and 113 µM. The aqueous micelles aggregated from $PEGPPh_2$-FpR agglomerate into suspensions, which is similar with the solution behaviour of Brij® surfactants, the organic analogue without the Fp junction. The redox activity of Fp in **1-4**, which is sensitive to assembling structures,will be a possible advantage for further investigation on this agglomeration behaviour.

KEYWORDS: metal-carbonyl complex; organometallic amphiphiles; Fp-surfactants; migration insertion reaction; iron-phosphine amphiphiles; iron-carbonyl PEG amphiphile

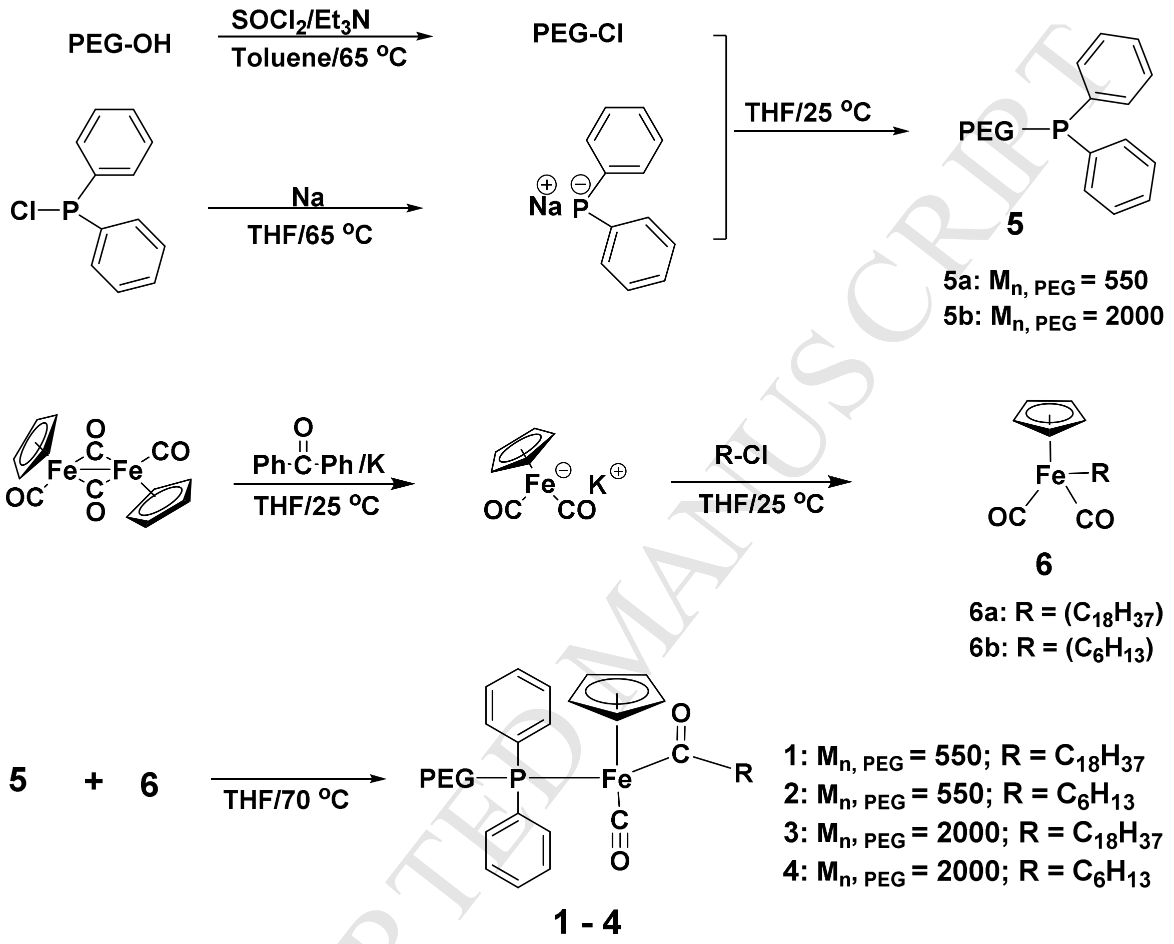
1. Introduction

Metal carbonyl (MC) complexes have been explored for biomedicine applications.[1-7] The strong IR absorption of the CO groups at the wavelengths between 1800 and 2200 cm^{-1}, a biologically transparent window, renders the complexes useful as vibrational probes for biosensors[1, 5] cell imaging[7] and bioassay[2], etc.[1],[5] The CO molecules released from MC complexes have functions of anti-bacteria,[8] and anti-inflammation[6]. However, MC complexes are normally unstable and insoluble in water.[3, 6] Supramolecular[9] and colloidal chemistry[3, 4] have been explored to address these challenges.

Taking advantage of well-studied migration insertion reaction (MIR),[10-13] we have recently synthesized a number of air-stable $CpFe(CO)_2$ (Fp) derivatives including small molecules [14-17] and macromolecules.[18-21] These molecules are able to assemble in water resulting in colloids stabilized by water-carbonyl interactions.[15-17, 22] The association of the highly polarized CO groups provides an aggregation-induced local electric field, which results in a significant enhancement in the IR signal of the CO groups.[14-17] To extend this research for potential biomedical applications, synthesis and self-assembly of Fp amphiphilic molecules, $PEGPPh_2$-FpR ($PEGPPh_2$ = polyethylene glycol, $M_{n,\,PEG}$ = 550 or 2000 g/mol; R = octadecyl or hexyl; Fp = $CpFe(CO)_2$) are designed and performed. These molecules are expected to assemble in water into MC colloids with a biocompatible PEG shell[3, 4] and functions derived from the aggregation of the Fp groups. The synthesis, characterization and preliminary investigation on the solution behavior of PEG-PPh_2-FpR are reported in this article.

2. Results and discussion

2.1. Synthesis and characterization of amphiphiles 1-4



Scheme 1. Schematic illustration for the synthesis of PEGPPh$_2$-FpC$_n$ amphiphiles.

The synthetic protocol for the preparation of PEGPPh$_2$-FpC$_n$ (**1-4**) is depicted in Scheme 1. PEG-Cl is converted from PEG-OH (Figure S1),[23, 24] and subsequently reacts with diphenyl phosphine sodium (PPh$_2$Na), which results in the generation of PEGPPh$_2$ **(5)**.[18] FpC$_n$ (**6**) is prepared *via* the reaction of cyclopentadienyldicarbonyliron potassium (FpK) with corresponding alkyl halide (Scheme 1). Subsequently, migration insertion reaction (MIR) of **6** in the presence of **5** was performed in THF at 70 ^{o}C for three days. After purification, the product was characterized using electrospray ionisation mass spectrometry (ESI-MS), NMR and IR spectroscopes. The ESI-MS spectra indicate that PEG segments with mixed degree of polymerization (DP) are incorporated in the amphiphiles (Figure S7-S10). ^{31}P NMR spectra (Figure 1) depict that the phosphine signal due to **5** at -20.2 ppm is totally disappeared and a peak at 69.5 ppm due to the coordinated phosphine appears suggesting that the MIR occurs.[18]

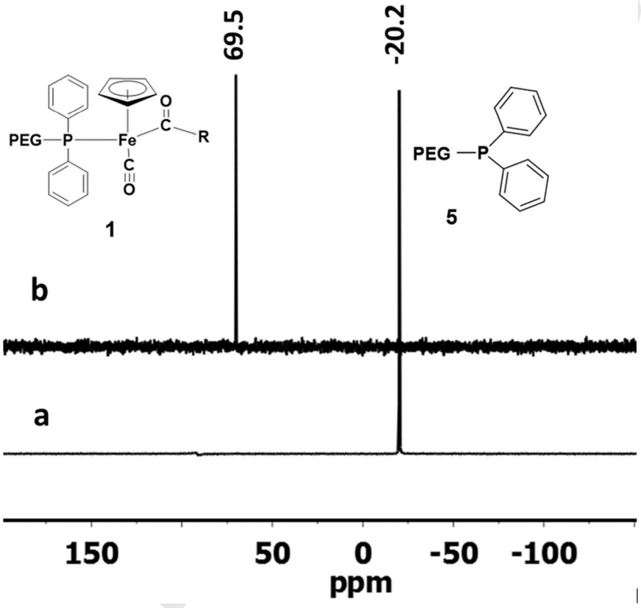


Figure 1. ^{31}P NMR ($CDCl_3$, 25 ^{o}C, 300 MHz) spectra for (a) **5** and (b) **1**

The success of the MIR was also proved by FT-IR spectroscopy. As shown in Figure 2, FT-IR spectrum for **6** shows two peaks at 1934 and 1990 cm^{-1} corresponding to the symmetric and asymmetric stretching of the two terminal carbonyl groups, respectively. After MIR, the two peaks are shifted towards lower frequencies and are observed at 1912 and 1607 cm^{-1} corresponding to the terminal and acyl CO groups, respectively (Figure 2). Particularly, the appearance of the frequency at a low wavenumber (1607 cm^{-1}) indicates the formation of metal-acyl bond resulting from MIR.[18]

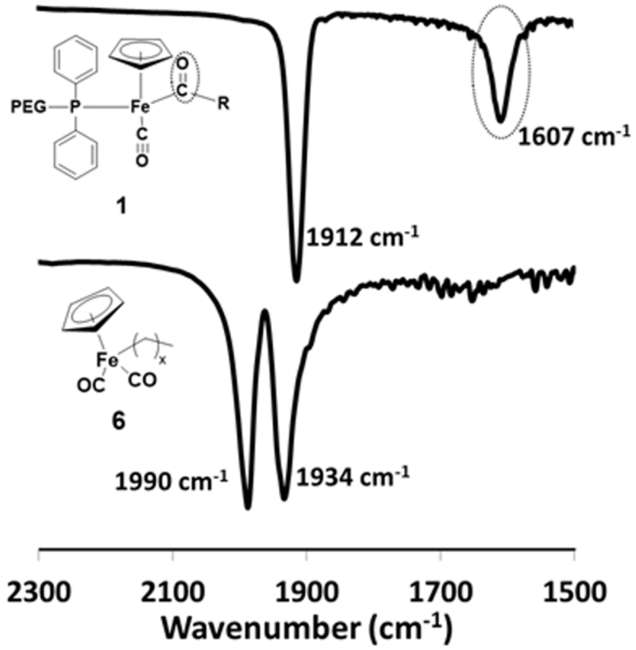


Figure 2. Partial FT-IR (KBr pellet) spectra of (a) **6** and (b) **1** before and after the migration insertion reaction.

^{1}H NMR spectra for **1** and **6** are compared in Figure 3. As shown in the figure, the upfield chemical shift for Cp protons from 4.71 in **6** to 4.36 ppm in **1** confirms that MIR occurred.[18] The appearance of the signals due to PEG chains in the spectrum for **1** indicates that **5** has coordinated with **6** as a result of the MIR. In addition, the chemical shift at 1.4 ppm for the methylene protons, α to iron, in **6** downfield shifts and splits into two peaks at 2.61 and 2.85 ppm in the spectrum of **1** (inset in Figure 3). The splitting of the signal is caused by the chiral center of iron in **1**, which further supports the occurrence of MIR.[18]

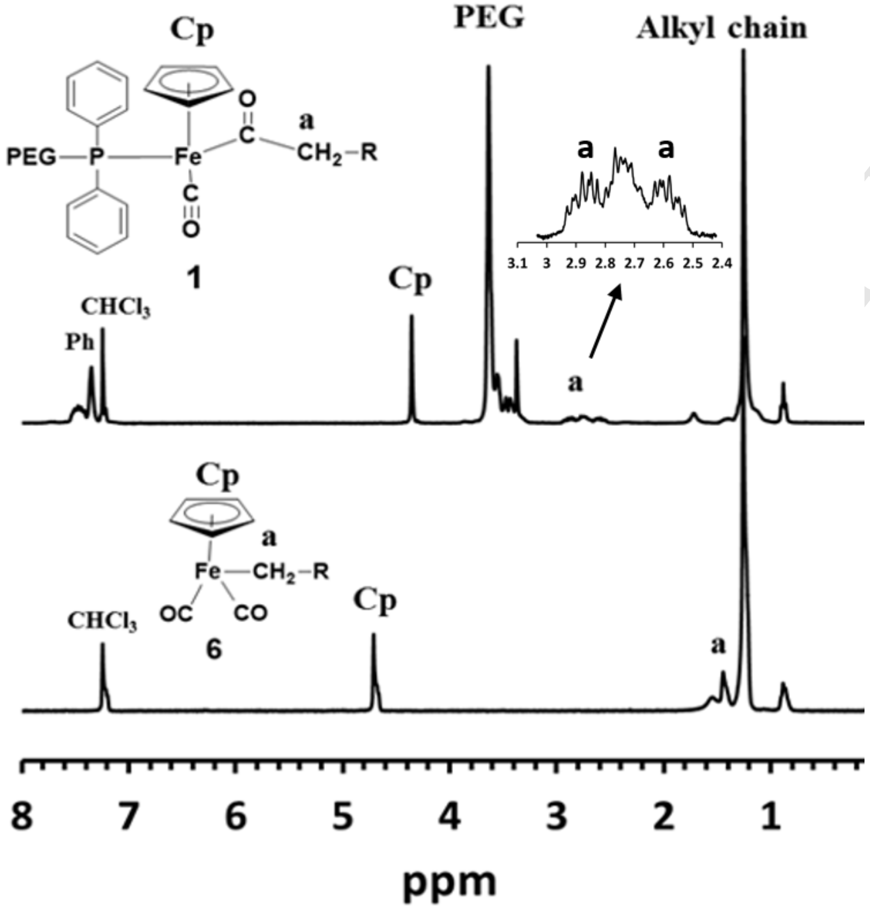


Figure 3. ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz) spectra for **6** (down) and **1** (up).

The synthesized amphiphiles are soluble in most organic solvents, e.g. THF, DCM, DMF, and stable in air over several months. The molecules also exhibit electrochemical stability. As shown in Figure 4 and S2, the cyclic voltammetry (CV) experiments of **1**-**4** in DMF reveal that the anodic and cathodic currents are reversible with oxidation peaks appearing at ca. 0.60 V (for **1** and **2** with shorter PEG chain) and ca. 0.55 V (for **3** and **4** with longer PEG chain), and with reduction peaks appearing at ca. 0.44 V (relative to Ag electrode).

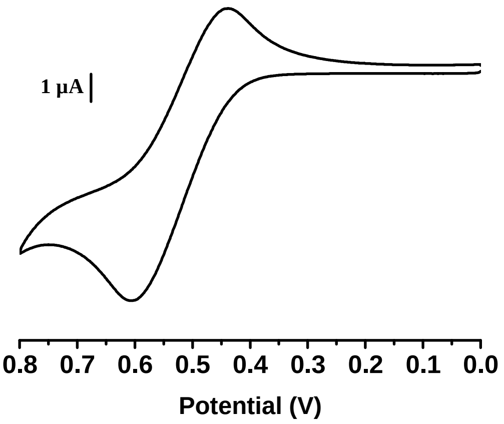


Figure 4. The CV curve (relative to silver electrode) for **1** in DMF solution with TBAP as electrolytes (scan rate 50 mV/s).

2.2. Amphiphilic behaviour of 1-4

As indicated by surface tension measurements, the surface tensions of the aqueous solutions of **1-4** gradually decrease with increasing concentrations and eventually reach constant values (less than 45 mN/m) at concentrations known as critical micelle concentrations (CMC) (Figure S3). The CMC values for **1-4** are summarized in Table 1. As shown in Table 1, the CMC value for **1** and **2** with a shorter hydrophilic PEG (M_n = 550 g/mol) is 29.9 ± 2.3 and 40.0 ± 6.2 μM, respectively. These values are lower than that for **3** (82.1 ± 4.5 μM) and **4** (113.3 ± 23.0 μM) with a longer PEG (M_n = 2000 g/mol). For the molecules with the same PEG chain length (**1** *vs* **2** or **3** *vs* **4**), the larger the hydrophobic alkyl group; the smaller the CMC values (Table 1). These results suggest that **1-4** are typical amphiphilies, because the molecules with shorter hydrophilic segments and longer hydrophobic chains result in stronger hydrophobic interactions of the alkyl chains and consequently a lower CMC.[25-27]

The maximum surface excess concentration (Γ) is calculated from the slope ($\partial\gamma/\partial logC$) of surface tension ($\gamma$) as a function of $logC$ (C < CMC) using Gibbs adsorption equation (Figure S3 in SI),[27, 28] from which the area per molecule (A) occupied at the water/air interface is calculated using the formula $1/(\Gamma \times N_A)$, where N_A = Avogadro's number. The results are included in Table 1 for comparison. As shown in Table 1, the *A* for **1** and **3** with a C_{18} group is 41.3 and 52.9 Å^2, respectively. These values are close to the dimensions of the Fp junction, which is ca. 49 Å^2 as estimated from a crystal structure of Fp derivative.[14] It suggests that **1** and **3** are compactly packed at the water/air interface due to a stronger hydrophobic interaction between C18 groups.[27] The molecule weight of PEG in **1** is 550 g/mol, which is shorter than that in **3** (2000 g/mol), so the relatively larger *A* for **3** is caused by the steric repulsion of flexible PEG_{2000} in water. This effect of PEG length on *A* is also observed, when **2** with PEG_{550} (A = 91.8 Å^2) and **4** with PEG_{2000} (A = 132 Å^2) are compared. The *A* values for **2** and **4** with a C_6 group are obviously larger than those for **1** and **3** with a C_{18} group, because the hydrophobic interaction between C_6 groups is smaller. The solution behaviour indicates that the shorter alkyl group has weaker hydrophobic interactions and thus larger CMC (Table 1).

Table 1. Critical micelle concentration (CMC) and area per molecule (*A*) occupied at the water/air interface of **1-4** in water.*

Molecules	CMC (μM)	Γ x 10^6 (Mole/m^2)	Area/molecule (Å^2)
(1) PEG_{550}-Fp-C_{18}	29.9 ± 2.3	4.023	41.3
(2) PEG_{550}-Fp-C_6	40.0 ± 6.2	1.809	91.8
(3) PEG_{2000}-Fp-C_{18}	82.1 ± 4.5	3.137	52.9
(4) PEG_{2000}-Fp-C_6	113.3 ± 23	1.25	132

* The date are calculated from surface tension measurements

2.3. Aqueous behaviour of 1-4

To investigate the assembling behavior of **1-4** in water, the aqueous solutions with 2.0 mg/mL of **1-4** were prepared and characterized using dynamic light scattering (DLS). The hydrodynamic diameters (D_h) for the micelles assembled from **1** and **2** increase within a few days after preparation. As shown in Figure 5a and b, the D_h for the solutions increases on the second day, but there are a significant amount of micelles with smaller D_h. On the 7th day, the smaller D_h disappears and only larger agglomerates are measurable. The colloids assembled from **3** and **4** with longer PEG_{2000} are relatively stable within 7 days, but also grow into larger one in a month (Figure 5 c, d). All micelles assembled from **1**-**4** eventually agglomerated into cotton-like suspensions that could be re-dispersed upon shaking.

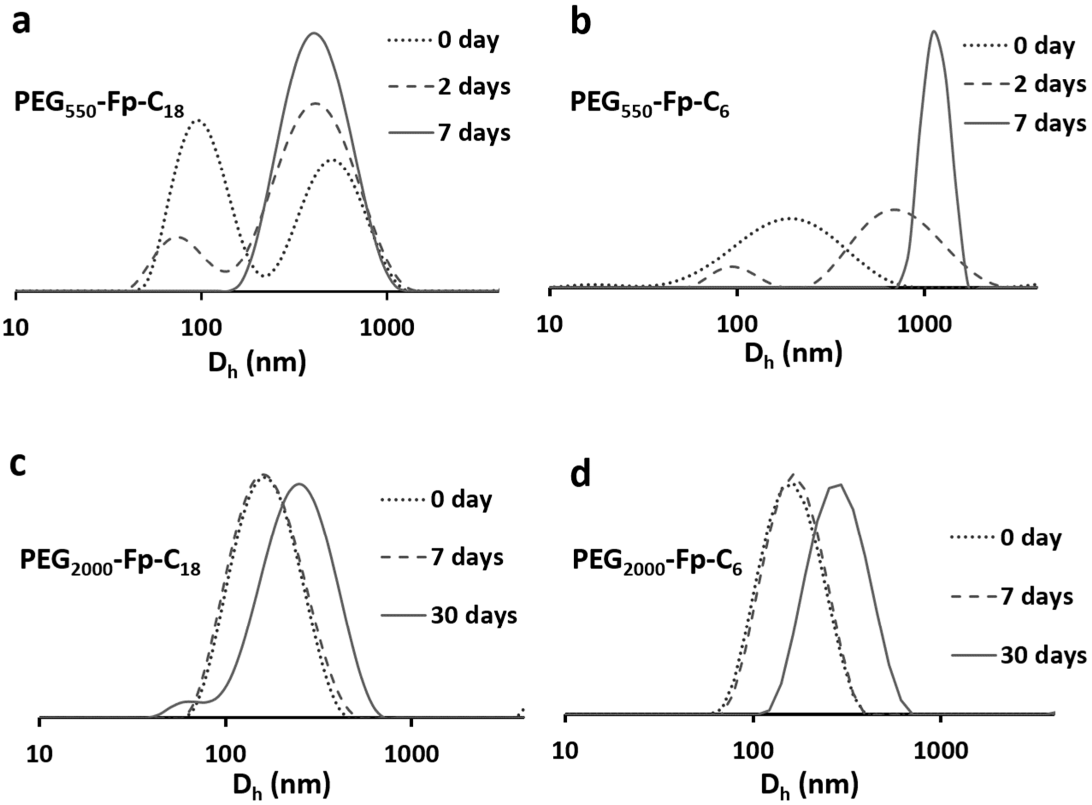


Figure 5. DLS curves for the aqueous solutions of **1- 4** over time.

Figure 6 compares the time when the cotton-like suspension appears for the aqueous solution of **1 – 4**. As shown in Figure 6, it takes much longer time for the solution of **3** and **4** due to the shielding effect of the PEG_{2000} chains. The agglomeration of **1** and **3** with a C_{18} group is relatively slower as compared with **2** and **4** with a C_6 group, suggesting that the stronger hydrophobic interaction of C_{18} groups slows the agglomeration rate. This agglomeration behaviour is also known for their organic analogue without Fp-junction, e.g. Brij® S10 ($C_{18}H_{37}$-b-PEG_{10}), which has been used for a variety of biomedical applications such as drug delivery.[29-31] Hydrophobic interaction is commonly used to explain this agglomerations behaviour.[32, 33] Further investigation to understand this behaviour will be performed using **1-4** by taking advantage of the Fp junction.

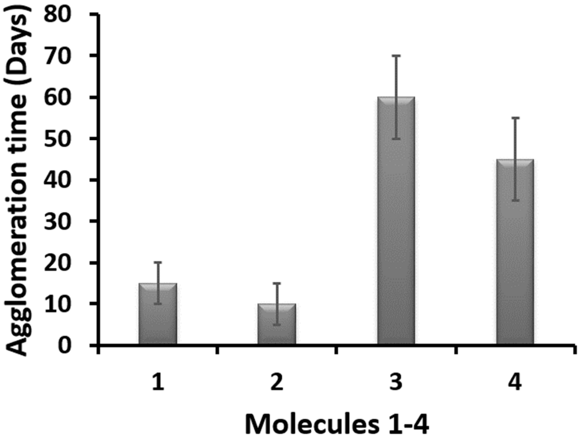


Figure 6. The time required for **1 – 4** in water (2 mg/mL) to agglomerate into suspension.

3. Conclusion

The first example of organometallic amphiphile with an Fp junction, $PEGPPh_2$-FpR, was prepared via migration insertion reaction of Fp alkyl derivatives in the presence of $PEGPPh_2$. The prepared macromolecules are stable in air and have a reversible redox activity in DMF. Surface tension measurements indicate that the prepared molecules exhibit typical amphiphilic behaviour with critical micelle concentrations (CMC) in water ranging from 0.03 to 0.113 mM depending on the chemical structure. The prepared aqueous micelles agglomerate over time into re-dispersible cotton-like aggregates. Their organic analogues without Fp junction (Brij® amphiphilic molecules) have similar agglomeration behavior, suggesting that the Fp junction has little effect on the solution behaviour of PEGPPh$_2$-FpR. Further research to investigate the agglomeration behaviour of the molecules by taking advantage of the redox activity will be performed.

4. Experimental Section

4.1. Materials and instrumentations

1-Chlorooctadecan (> 98.0%), and thionyl chloride (≥ 99.0%) were purchased from TCI America and Fulka Analytical, respectively. 1-bromohexane (> 98.0%), Cyclopentadienyliron (II) dicarbonyl dimer (99%), triethylamine (≥ 99%), Chlorodiphenylphosphine (98%), benzophenone (99%) and poly(ethylene glycol) methyl ether (PEG, M_n = 550 and 2000), were purchased from Sigma-Aldrich and used as received. Potassium metal (99.5%, rods in mineral oil) and sodium metal (99.9%, cubs in mineral oil) were purchased from Sigma-Aldrich, cut into small pieces and washed in hexane before using. Tetrahydrofuran (THF) was distilled over sodium/benzophenone before use. All other solvents were obtained from local commercial providers and used as received.

^{1}H and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on Bruker-300 (300 MHz) spectrometer at room temperature using appropriate solvents as reported in each case. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 spectrophotometer with a resolution of 1 cm^{-1} at room temperature. Samples were prepared using

KBr pellets by grinding and compressing of the amphiphile in anhydrous KBr using Nujol mulls. Electrospray ionisation mass spectrometry (ESI-MS) were performed using a Thermo Scientific Q Exactive mass spectrometer. Molecules **1 – 4** were dissolved in acetonitrile with 0.4 w% formic acid and the solutions were infused at 10 µL/min with spray voltage of 3.2 kV and capillary temperature of 280 ^{o}C. Dynamic light scattering (DLS) experiments were performed at 25 °C using Zetasizer Nano Series (Nano-S90, Malvern Instruments) with laser wavelength of 633 nm at fixed angle of 90^{o}. Surface tension of pure water and the aqueous solutions of the prepared metallo-amphiphiles with different concentrations were measured at 22 ^{o}C using tensiometer Data Physics DCAT 21 system. Cyclic voltammetry (CV) measurements were obtained using DY2000 Multi-Channel Potentiostat (Digi-Ivy Inc.) workstation with a scan rate of 50 mV/sec and silver wire as a reference electrode. All samples were measured in DMF using tetrabutylammonium perchlorate (TBAP, 2mg/mL).

4.2. Synthesis of 1-4.

Synthetic procedures of **1** (PEG_{550}-Fp-C_{18}) that contains PEG (M_n = 550 g/mol) and octadecyl chain, as representative amphiphile, is discussed in details in this section. All synthesis steps were conducted under dry N_2 atmosphere using Schlenk line techniques.

4.2.1. Synthesis of (5)

Synthesis of PEG_{550}-Cl.[24, 25] A toluene solution (17 mL) of poly(ethylene glycol) methyl ether, M_n = 550 (2.0 g, 3.6 mmol) and triethylamine $(C_2H_5)_3N$ (0.40 g, 4.0 mmol) was added dropwise into a 100-mL Schlenk flask containing thionyl chloride $SOCl_2$ (2.60 g, 22 mmol) at 0 ^{o}C (ice bath). After the addition, the ice bath was replaced with oil bath and the solution is gradually heated up to 65 °C. After stirring at 65 °C overnight, the solution was passed through a celite column to remove the resulted triethylamine hydrochloride salt and the filtrate was subject to rotary evaporation to remove toluene. The crude product was then dissolved in a minimal THF and precipitated out in hexane as cloudy oil. The final product was collected and dried under vacuum, yield PEG_{550}-Cl (1.74 g, 71%). ^1H NMR (300 MHz, $CDCl_3$, δ): 3.75 (t, 2H, $-CH_2Cl$), 3.55-5.65 (s, 44H, CH_2CH_2O), 3.50 (t, 2H, - O - CH_2- CH_2Cl), 3.37 (s, 3H, CH_3O). ^1H NMR results for PEG_{2000}-Cl as follow. ^1H NMR (300 MHz, $CDCl_3$, δ): 3.74 (tbr, 2H, $-CH_2Cl$), 3.58-5.68 (sbr, 176H, CH_2CH_2O), 3.54 (brt, 2H, - O - CH_2- CH_2Cl), 3.37 (s, 3H, CH_3O).

Synthesis of $NaPPh_2$.[18, 21] Sodium diphenylphosphide ($NaPPh_2$) was prepared as previously reported by our group. ^{31}P NMR (300 MHz, THF, δ): -20 (s,1P, Ar_2PNa)

Synthesis of PEG_{550}-PPh_2 (5a). PEG_{550}-Cl (1.01 g, 1.78 mmol) was added to a 100-mL Schlenk flask and dissolved in dry THF (5 mL). The flask was placed in an ice bath. To the flask, 5.5 mL sodium diphenylphosphide solution (0.55 g, 2.65 mmol; excess) was added dropwise. The resulting mixture was left under stirring for 2 hours. Then, degassed methanol (2 mL) was added dropwise to react with the excess sodium diphenylphosphide. As a result, the color of the solution was changed from deep red to pale yellow. After the solution was passed through a celite column, the mixed solvents of THF/methanol were removed under vacuum, leaving pale yellow oil as crude product. The crude product was dissolved in a minimal THF and subsequently precipitated out in degassed hexane. After this step of purification, the final product was collected and dried under vacuum, yield 0.89 g (69.6 %). ^{31}P NMR (300 MHz, $CDCl_3$, δ): -21 ppm; ^{31}P NMR (300 MHz, THF, δ): -19 ppm; ^1H NMR (300 MHz, $CDCl_3$, δ): 7.15, 7.55 (sbr, 10H, ArH), 3.48 (sbr, 48H, CH_2CH_2O), 3.20 (s, 3H, CH_3O).

4.2.2. Synthesis of (6)

Fp-C_n (**6**) was synthesized by coupling of cyclopentadienyldicarbonyliron potassium (FpK),[34] with 1-chlorooctadecane for **6a** or 1-chlorohexane for **6b**. For **6a**, under stirring at 0 °C, a solution of $C_{18}H_{37}Cl$ (2.5 cmL, 7.3 mmol) in THF (5 mL) was added to an orange suspension of FpK (2 g, 9.3 mol) in THF (20 mL). The orange suspension gradually turned to brown and was kept stirred at room temperature for 2 hours. THF was then removed by rotary evaporation and the residue was extracted using degassed hexane. The supernatant was collected and rotary evaporated. The resulting solid was chromatographed using a plug of silica column and degassed hexane/DCM (4:1 v/v) are used as eluent. The first yellow band was collected and solvents were removed using rotary evaporation. The bright yellow crystals were collected and dried under vacuum. Yield 2.8 g (89.2 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.71 (s, 5H, Cp ring), 1.44 (br, 2H, Fe-CH_2-alkyl chain), 1.25 (br, 32H, CH_2-alkyl chain), 0.87 (t, 3H, terminal CH_3); FT-IR (KBr): ν =1990 and 1934 cm^{-1} (two CO groups stretching).

4.2.3. Synthesis of PEG$_{550}$PPh$_2$-FpC$_{18}$ (1)

A solution of **5a** (1.0 g, 1.39 mmol) and **6a** (0.72 g, 1.7 mmol) in THF (60 mL) was prepared in a 100-mLSchlenk flask. The solution was then heated up and refluxed at 70 ^{o}C for three days. THF was subsequently removed *via* rotary evaporation, resulting in a dark-brown crude product. The crude product was then suspended in a minimal amount of degassed hexane and transferred to a silica column. The column was first flushed using degassed hexane to remove the excess Fp-C_{18} (**6a**), and subsequently washed using dry THF. A dark brown band was collected. After removing solvent, viscous dark brown oil was collected and dried under vacuum, 1.27 g (79.5 %). ^{31}P NMR (300 MHz, $CDCl_3$, δ): 69.5 (Ph_2-P-C); ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.36 (s, 5H, Cp ring), 2.61 and 2.85 (m, 2H, acyl-CH_2-alkyl chain), 1.25 (br, 32H,

CH_2-alkyl chain), 0.87 (t, 3H, terminal CH_3), 3.6 (br, 42H, CH_2CH_2O), 3.37 (s, 3H, CH_3O), 2.78 (t, 2H, CH_2-P, overlapped), 7.2-7.4 (br, 10H, aromatic protons); FT-IR (KBr): ν =1912 cm^{-1} (terminal CO stretching), 1607 cm^{-1} (migrated acyl carbonyl), Figure 1-3. Molecule **2-4** are prepared and characterized in the same fashion as for **1**; detailed synthesis for **2-4** is described in the Supporting Information (Figure S4-S6).

4.3. Preparation of the micelles

Typical, 2.0 mg/mL aqueous solution is prepared by adding 10.0 mL of water into a THF solution of **1-4 (**20 mg in 0.5 mL THF) under stirring. Subsequently, THF was removed *via* either bubbling with N_2 for an hour or dialysis over night against water.

5. Acknowledgements

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Supporting Information Available:

Supplementary data related to this article, including additional synthesis procedure, NMR spectra, cyclic voltammetry and surface tension results, can be found at http://

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Synthesis and Solution Behaviour of Metal-Carbonyl Amphiphiles with an Fp ($CpFe(CO)_2$) Junction

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Highlights:

- Metallo-amphiphilic macromolecules with an iron-carbonyl junction are synthesised
- The prepared amphiphiles are redox active and able to self-assemble in water